

The challenge of emerging groundwater contaminants

Emerging contaminants, including a range of pharmaceuticals, industrial compounds and personal care and lifestyle products, are increasingly being found in groundwater but they are poorly understood.

What are emerging contaminants?

A large variety of trace contaminants are starting to be detected in groundwater at potentially environmentally significant concentrations. Such emerging contaminants (ECs) include not only newly developed compounds but also compounds newly discovered in the environment, in some cases due to analytical developments, and compounds that have only recently been categorised as contaminants. ECs include a host of different compounds including; pharmaceuticals and personal care products (PPCPs), pesticide metabolites/degradation compounds, veterinary products, industrial compounds/by-products, food additives as well as engineered nano-materials.

These types of compounds (largely organic) are used by society in huge quantities for many different purposes including, industrial manufacturing processes, human and animal healthcare, and the production and preservation of food, to list a just a few. In the last few decades there has been a growing interest in the occurrence of these ECs in the aquatic environment, their environmental fate and potential toxicity (Kümmerer, 2009). Due to the vast array of possible compounds, many published studies have selected ECs according to priority lists established, taking into account usage, predicted environmental concentrations as well as toxicological, pharmacological and physicochemical data (Hilton et al., 2003). To date the occurrence of ECs has been much better characterised in wastewater and surface water compared to groundwater.

Regulatory context

Monitoring of anthropogenic micro-organic pollutants in river basins is required within the framework of various national regulations within

the EU, with the overall aim of protecting and improving the quality of water resources. As part of achieving this, groundwater bodies have to be assessed as being at “good status”. In assessing status, threshold values (standards) have to be established for pollutants that put the groundwater body at risk of failing to achieve any of its environmental objectives. Whilst for many chemical pollutants there is sufficient information to establish threshold values, in the case of many ECs the paucity of knowledge on occurrence, toxicity, impact, and environmental behaviour mean that threshold values cannot yet be set. However, in the future, if ECs are found to lead to the risk of pollution of groundwater, and have the potential to compromise environmental objectives, then standards (threshold values) will be required. Overall, the number of compounds that are regulated, through drinking water standards and/or environmental quality standards, is likely to grow in the coming decades.

Major sources of ECs, and pathways to groundwater

Sources of ECs in the environment that may eventually impact groundwater can be divided into point-sources and diffuse sources of pollution. Diffuse sources originate from poorly defined sources that typically occur over broad geographical scales. Examples of diffuse source pollution include agricultural runoff from bio-solids and manure sources, storm-water and urban runoff, leakage from reticulated urban drainage systems and diffuse aerial deposition. Diffuse sources of pollution have higher potential for natural attenuation in the soil and subsurface and a lower environmental loading compared to point sources, but they can be poorly defined with less direct/obvious links back to the ‘polluter’. As such, it continues to be

a real challenge to monitor, regulate and assess their impact on groundwater resources.

In contrast, point sources of ECs originate from discrete locations, whose spatial extent/plume of pollution is therefore usually more constrained. Important examples include waste disposal sites (landfill sites, industrial impoundments, farm waste lagoons), industrial effluents (e.g. manufacturing plants, hospitals, food processing plants), resource extraction (mining), municipal sewage treatment plants and combined sewage-storm-water overflows, and septic tanks. Most published studies have focussed on point source pollution because this usually results in higher EC loading to a particular environmental receptor (surface water or groundwater body or aquatic species) and is easier to detect. Engineered solutions to point source pollution are perhaps more straightforward, are seen to deliver the greatest environmental benefit, and as such attract the greatest funding. There is a stronger historical legacy of regulatory control on point source pollution, and the connection between the pollution and the polluter is often easier to define.

Occurrence of ECs in groundwater

Loos et al. (2010) reported results from the first pan-European reconnaissance of 164 groundwater samples collected and analysed for persistent organic pollutants from 23 countries. The most frequently detected compounds included ECs such as DEET (insect repellent), caffeine, perfluorooctane sulfonate (surfactant formerly used in coatings and fire-fighting foam) as well as carbamazepine (mood stabilising drug) and metabolites of the commonly detected pesticide atrazine.

A recent review of world-wide EC occurrence in groundwater by Lapworth et al. (2012) demonstrated that nanogram-microgram per litre concentrations are present in groundwater for a large range of ECs, as well as metabolites

and transformation products. Under certain conditions this pollution may pose a threat to freshwater bodies for decades due to relatively long groundwater residence times, low potential for microbial breakdown and prevailing redox conditions. Overall, >180 different ECs have been detected in groundwater. Figure 1 summarises maximum EC concentrations found in groundwater (world-wide) for major groups of compounds: steroids and hormones; sweeteners and preservatives; 'life-style' compounds – e.g. caffeine; industrial compounds; personal care products (PCPs) and veterinary medicines. Table 1 summarises the occurrence of ECs in groundwater from regional and national reconnaissance studies.

Stuart et al. (2012) recently reviewed the types of ECs found in UK groundwater. Results from the Environment Agency for England and Wales showed 260 different organic pollutants were detected at more than 10 locations. There were frequent detections of the following ECs: caffeine (27%); DEET (10.6%), bisphenol A (plastics manufacture, 7.9%); carbamazepine (1.2%); triclosan (antibacterial agent, 0.8%). As an example, Figure 2 shows the widespread occurrence of caffeine in groundwater across England and Wales.



Antibiotics and other pharmaceuticals and health care products are typical of emerging contaminants (www.freeimages.co.uk)

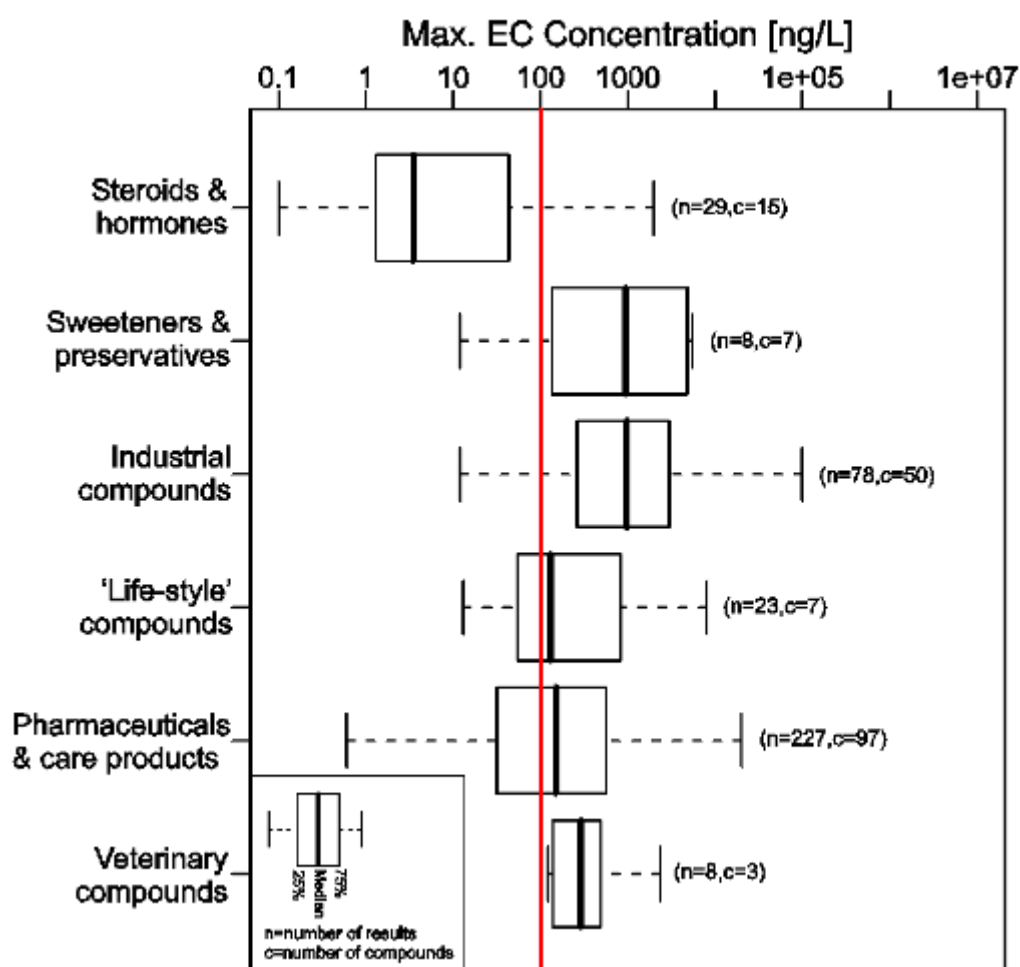
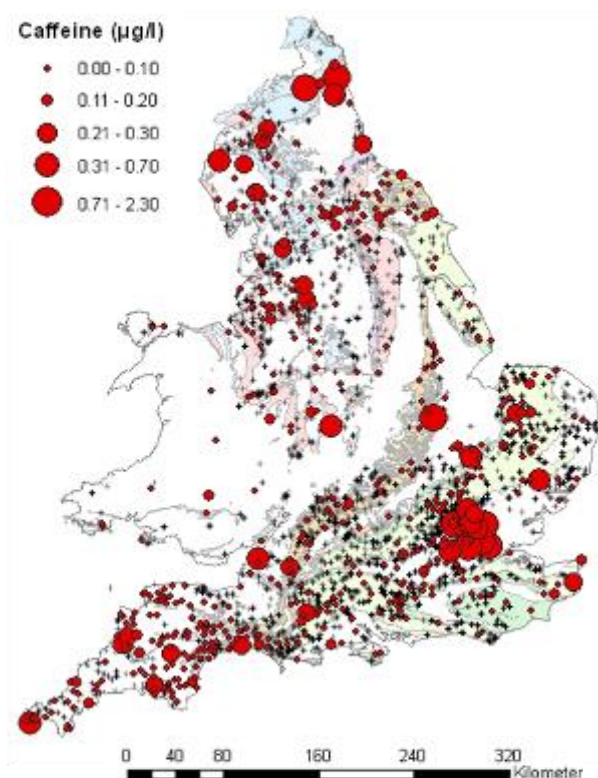


Figure 1. Box-plot of maximum EC concentration in groundwater (world-wide) for major groups of compounds. The red line shows the EU maximum acceptable concentration (100 ng/L) for individual pesticides in drinking water for comparison. Source: Lapworth et al. (2012)

Table 1. Occurrence of ECs in groundwater from selected published reconnaissance studies

Country	Study (sites, compounds*)	Maximum concentration (ng/L) /frequency (%)	Reference
England & Wales	Nation-wide survey (2644, >800)	DEET (6.5 ³ ng/L, 10.6%), bisphenol A (9.3 ³ ng/L, 7.9%), carbamazepine (3.6 ³ ng/L, 1.2%), triclosan (2.1 ³ ng/L, 0.8%), caffeine (4.5 ³ ng/L, 27%), nicotine (8 ³ ng/L, 4%), ibuprofen (290 ng/L, 0.3%).	Stuart et al. (2011)
France	Rhône-Alpes (70,51)	Salicylic acid, carbamazepine, and testosterone (100%), paracetamol and androstenedione >90%, diclofenac and sulfamethoxazole > 60%	Vulliet and Cren-Olivé (2011)
Germany	Baden-Württemberg (105,60)	β-blockers, analgesics, carbamazepine, diclofenac, antibiotics iopamidole (>10 ng/L)	Sacher et al. (2001)
USA	Nation-wide survey (47,65)	DEET (35%), bisphenol A (30%), tri(2-chloroethyl) phosphate (30%), sulfamethoxazole (23%) 4-octylphenol monoethoxylate (19%)	Barnes et al. (2008)

*Number of compounds screened for in samples



in groundwater across England and Wales. Source: Stuart et al. (2011)

Future challenges

A large variety of ECs are detected in groundwater at potentially environmentally significant concentrations as a result of both recent and historical activities. However, compared to other freshwater resources the occurrence of ECs in groundwater is poorly characterised. Recent studies have shown that important groups of ECs include a range of pharmaceuticals and personal care products, industrial and life-style compounds. Presently, very little is known about the occurrence and fate of anthropogenic nano-materials in groundwater, but this newly emerging group of contaminants will warrant further research in the future. To date, many national and regional studies have been biased towards potentially contaminated sites so the actual frequency and distribution in groundwater remains largely unknown. More systematic regional-scale studies are needed to assess the spatial and temporal occurrence of ECs in groundwater. In

the coming decades, a growing number of ECs are likely to have drinking water standards, environmental quality standards and/or groundwater threshold values defined, and so a better understanding of the spatial and temporal variation remains a priority.

Dan Lapworth and Marianne Stuart
Groundwater Science Programme
British Geological Survey

References

- Barnes, K., Kolpin, D., Furlong, E., Zaugg, S., Meyer, M., Barber, L., 2008. A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States I. Groundwater, *Science of the Total Environment* 402, 192-200.
- Hilton, M., Thomas, K.V., Ashton, D., 2003. Targeted monitoring programme for pharmaceuticals in the aquatic environment. UK Environment Agency R&D Technical Report P6-012/6, Environment Agency, UK.
- Kümmerer, K., 2009. The presence of pharmaceuticals in the environment due to human use—present knowledge and future challenges. *Journal of Environmental Management* 90, 2354-2366.
- Lapworth, D.J., Baran, N., Stuart, M.E., Ward R.S., 2012. Emerging contaminants in groundwater: A review of sources, fate and occurrence. *Environmental Pollution* 163, 287-303.
- Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M., Gawlik, B.M., 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Res.* 44, 4115-4126.
- Stuart, M.E., Lapworth, D.J., Crane, E., Hart, A., 2012. Review of risk from potential emerging contaminants in UK groundwater. *Sci. Tot. Env.* 416, 1-21.
- Stuart, M.E., Manamsa, K., Talbot, J.C., Crane, E.J., 2011. Emerging contaminants in groundwater. British Geological Survey Open Report, OR/11/013. 6pp.
- Sacher, F., Lange, F.T., Brauch, H.-J., Blankenhorn, I., 2001. Pharmaceuticals in groundwaters. Analytical methods and results of a monitoring program in Baden-Württemberg, Germany. *Journal of Chromatography A* 938, 199-210.
- Vulliet E., Cren-Olivé C., 2011. Screening of pharmaceuticals and hormones at the regional scale, in surface and groundwaters intended to human consumption, *Env. Poll.* 159, 2929-2934.